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A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
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I. Introduction

Rhenium has been discovered comparatively recently, consequently not a great deal is known about it. Its physical properties offer many interesting possibilities, therefore any ores containing rhenium would be of considerable value. Its close relationship to manganese in the periodic table led to the belief that manganese ores would be an excellent place to search for the metal. Investigation of the literature of rhenium revealed that no ore was known to contain more than 0.001 per cent of rhenium, but due to the volatility of the oxide a concentration might be expected in the flue products of metallurgical operations.

With this knowledge an investigation of flue dust from the Domestic Manganese and Development Co. Plant at Butte, Montana and some flue dust from the Great Falls Plant was undertaken to determine whether or not rhenium was present in these.

The problem involved a very careful study of all the available literature. Therefore a review of the important features connected with the element may be a helpful and instructive addition to this thesis.

II. History

While preparing his periodic table, Mendeléeff found no known element to occupy the place of what is now element No. 75. He therefore prophesied the existence of an element and called it dwi-manganese. In 1925 Ida and Walter Noddack, German chemists, discovered the missing element and called it rhenium after the German province, the Rhine. They examined,

spectrographically, 30 complex minerals in five of which they believed they found rhenium.(12) By the treatment of one kilogram of columbite they were able to obtain 50 milligrams of a product containing 5 per cent rhenium and masurium.

Priority of discovery was claimed by J. G. F. Druce, who with his co-workers, claimed he found rhenium as a frequent impurity in manganese salts. Subsequent work, however, showed no rhenium was present in manganese salts.

III. Occurrence of Rhenium in Nature

Ida and Walter Noddack have estimated that the earth's crust contains 10^{-12} of rhenium as compared to iron of 10^{-2}. It has been found in many complex minerals such as: gadolinite, columbite, tantalite, molybdenite, wolframite, etc.

Of 1600 minerals examined by the Noddacks they found rhenium to be present in 100 of them. However, in their investgations they found no mineral to contain more than 0.001 per cent rhenium.

Commercially rhenium has been obtained from molybdenite. The chief present supply is from certain un-named copper refinery slimes.(3) In these slimes rhenium occurs to the extent of 50 p.p.m., thus the rhenium content exceeds that of platinum in some of these slimes.

In a plant of the Vereinigte chemische Fabriken at Leopoldshall near Magdeburg, Germany rhenium is obtained from waste metallic products. In this the rhenium occurs to the extent of one part in 60,000 parts of raw materials. In the article (12) by W. Feit a picture is shown of an enormus pile

of raw material from which will be extracted 5 to 6 pounds of rhenium as potassium perrhenate.

IV. Rhenium Products and Metallic Rhenium

A. Identification and Analysis

1. Spectrum

Since rhenium yields characteristic lines in the spectrum, these constitute the easiest and readiest means of identifying the element. The test is so delicate that only one part in ten million may be detected.

2. Alkali Melt

In the absence of chromium, manganese, ruthenium, and osmium almost any residual material containing rhenium in amounts of 0.5 per cent or more forms a yellow-colored melt when fused with caustic alkali. The rhenium may be extracted from the melt by water and affords an easy separation of most metals except arsenic and molybdenum. Yagoda(4) says that rhenium may also be detected in the sodium carbonate bead providing manganese is not present in over 50 per cent of the sample. It has a characteristic color change of from black to yellow to white with corresponding time intervals of one minute for the black and ten minutes for the disappearance of the yellow.

3. Colorimetric Analysis

To a hydrochloric acid solution of a perrhenate stannous chloride and potassium thiocyanate are added which produce a yellow-brown thiocyanate (5). This color may be extracted by ether or ethyl acetate to produce a rose colored extract.

By carefully preparing standards a very close approximation of the rhenium content of the sample may be had by comparison. Snell claims that as low as 0.001 milligram of rhenium may be detected by this method.

B. Separation and Detection of Rhenium in Various Schemes of Analysis

In the Prescott and Johnson System of Analysis the rhenium is found in the arsenic group if sufficient time is allowed for precipitation(6). It has, however, been found that in solutions containing less than 4 per cent hydrochloric acid by weight rhenium is not quantitatively precipitated by hydrogen sulphide (6). However, in solutions containing 33 per cent hydrochloric acid by weight the rhenium is precipitated quantitatively (6). By having the solution 33 per cent hydrochloric acid it was found from actual tests that the precipitation by hydrogen sulphide was very rapid and complete. Also the precipitation in the hat solution was accompanied by very characteristic color changes. The solution changed a pinkish color after a short passage of hydrogen sulphide then gradually, after several minutes, changed to a purple. When a good purple color was obtained, the Re_2S_7 precipitated out quickly as a black, flocculant precipitate.

In the Noyes and Bray System of Analysis the bulk of the rhenium is found in the rhodium-iridium filtrate of the tellurium-copper group.

C. Extraction and Preparation of Rhenium

Quite a number of processes for recovering rhenium have

been patented, but commercial production is now confined to the treatment of a complex, sulphide slime as a by-product from an unstated metallurgical process (2). The slime is weathered in air for many months then leached in water to extract a brownish-green solution of rhenium, copper, nickel, cobalt, zinc, etc. By adding ammonium sulphate in carefully gauged amounts and evaporating nickel, cobalt, copper, and zinc are removed. Several repeated operations are required and then the rhenium is recovered by fractional crystallization. The rhenium is recovered as potassium perrhenate. By repeating the recrystallization process twice, a final product containing 64.6 per cent rhenium may be obtained, which is pure $KReO_4$.

Rhenium may also be recovered by fractional sublimation (2). This is done by reducing the sulphides with hydrogen at 800°C followed by heating in a stream of oxygen at 150°C. Re_2O_7 and Re_2O_8 are formed and sublime. By several sublimations a fairly pure Re_2O_7 and Re_2O_8 are obtained which can easily be reduced to the metal.

D. Production of Rhenium

Rhenium was discovered in 1925, but as late as the summer of 1929 only 3 grams had been separated. The total quantity produced by the end of 1930 was in the neighborhood of 300 pounds. Germany is at present able to produce about 440 pounds a year.

Compared to other rare and newly discovered elements, rhenium is quite cheap. In 1931 the price was around $6.00

a gram, where as today it may be bought for around $45.00 an ounce.

V. Chemistry and Physics of Rhenium

A. Chemical and Physical Properties of Rhenium Metal and Some Rhenium Compounds

1. Rhenium Metal

Rhenium is a member of group No. VII in the periodic system and resembles manganese. It is a silvery-white metal, similar to platinum, is stable in air, and is the least fusible of all metals except tungsten. The metal is very little affected by hydrofluric acid or hydrochloric acid. Sulphuric acid dissolves it slowly, while nitric acid readily dissolves rhenium. Sintered rhenium is ductile in the cold and when warmed it can be forged, hammered, and rolled.

Physical and Chemical Properties of Rhenium

Atomic number.....75

Atomic weight..... 186.3

Specific gravity..... 20.53-21.33

Crystal structure..... Hexagonal system

Color..... Silvery-white

Hardness (Brinell)..... 250

Melting point..... 3100°C

Boiling point..... Unknown

Specific heat 0° to 20°C..... 0.0346

Coeff. of thermal expansion perpendicular to c axix

0.0_5467

Along c axis..... 0.0_41245

Characteristic spectrum lines..... 3465 A^{o} (ultra violet), 4889 A^{o} (Blue), 5271 A^{o} (Green)

Electrical resistance..... 4 times W.

2. Rhenium and Oxygen

Rhenium has many oxides of which Re_2O_7 is the most stable. it is formed by heating the metal in oxygen. The oxide condenses from a colorless gas to a yellow liquid at 350°C and becomes solid at 220°C forming yellow crystals in the shape of hexagonal plates. The melting point of Re_2O_7 is depressed by water, but no hydrates have as yet been found. Aqueous solutions of Re_2O_7 have the characteristics of an acid. The reaction is believed to be as follows:

$Re_2O_7 + H_2O = 2HReO_4$. It dissolves metal hydroxides and can be neutralized by bases with the development of heat. Oxidizing agents show no effect on an aqueous solution of Re_2O_7. Mild reducing agents show no perceptible action, while strong ones color the solution.

Re_2O_5, a purple oxide, has been prepared by reducing Re_2O_7 with Re. This oxide is insoluble in water, dilute hydrochloric acid, or sulphuric acid, but dissolves in warm, dilute nitric acid.

Re_2O_3 is a reddish oxide but has not yet been isolated. ReO_2 is black and can be formed by reducing perrhenates and rhenates with hydrogen. ReO_4 or Re_2O_8, white, has been formed by heating the metal in oxygen below 150°C.

The higher oxides of rhenium are acid forming, while the

lower are slightly basic.

3. Rhenium and the Halogens

When rhenium is heated in chlorine, it forms two, volatile chlorides namely: rhenium hexachloride, Re CL_6, and rhenium heptachloride, Re CL_7. Re CL_6 is in the form of brown needles, sublimes at 150°C, and is hydrolyzed in solution. Re CL_7 is green and more volatile. Dark colored bromides and iodides are also formed. Numerous potassium, silver, caesium, and thallous rhenium chlorides and bromides have been prepared.

4. Rhenium and Carbon

Rhenium does not react with carbon at a high temperature to form a carbide, nor does it react with carbon monoxide to form a carbonyl. Rhenium, however, forms a carbide when heated in methane.

5. Various Rhenium Compounds

The perrhenates are the most common rhenium compounds and are formed by neutralizing a solution of perrhenic acid with NaOH, KOH, etc. The perrhenates are soluble in water, They are colorless if made from a colorless base. They are very stable, and if the base is non-volatile, can be heated to redness in oxygen without decomposition. They are, however, decomposed by hydrogen.

B. Electro-Chemistry of Rhenium

The electrode potential of rhenium in an electrolyte of $2N\text{-}H_2SO_4$ is 0.6 volts more negative than the normal calomel electrode (1). This puts rhenium between copper and thallium

in the electrochemical series.

VI. Applications and Applicabilities of Rhenium Metal and Rhenium Alloys

A. In Chemistry

Rhenium in the form of potassium perrhenate has been recommended for the quantitative determination of potassium (8). This is better than that involving the perchlorate; the procedure is similar but less reagent need be used due to the greater molecular weight. The metal is also capable of catalyzing reduction and hydrogenation processes.

B. In Metallurgy

The tungsten-rhenium alloy diagram has been worked out which shows the solidus to have two eutectics: one at 2892°C and 50 atom per cent rhenium and the other at 2822°C and 67 atom per cent rhenium, and a maximum at 3005°C corresponding to W_2Re_3. (7)

A use has been sought for rhenium in radio tubes and in filaments of incadescent lamps. Its high melting point and hardness offer many attractive possibilities.

Rhenium may be deposited from both an acid or alkaline bath but involves a careful control of the hydrogen ion concentration, temperature, and current density (3). The metal may be plated on brass, copper, and other metals. It is also easily co-deposited with other metals such as cobalt and nickel. Rhenium plated tungsten filaments give a longer life and a higher resistance to attack by residual gases.

Rhenium has also begun to displace rhodium in rhodium-

platinum thermo-electric couples.

VII. Experimental Work

We first treated 250 grams of the manganese flue dust by dissolving 50 grams at a time in hydrochloric acid. The solution was made 2.5 N in hydrochloric acid and a hydrogen sulphide precipitation made. After the arsenic and other sulphides were taken out, the solution was diluted and another hydrogen sulphide precipitation made to take out the rest of the copper group.

These sulphides were kept and examined separately. Several portions of each were carried through the Noyes and Bray System down to the rhodium-iridium filtrate in which rhenium is reported to be found. The characteristic high acid sulphide precipitation and the colorimetric method of detection were both used to examine the filtrate. Neither of these showed any indication of rhenium being present.

Several tests of this colorimetric method of analysis(5) were made with a known potassium perrhenate solution which was obtained from Dr. Mathews of the University of Wisconsin. This test works very well and will serve to detect rhenium down to 0.001 mg.

Investigation of the literature showed that rhenium was precipitated by hydrogen sulphide in a 33 per cent by weight hydrochloric acid solution. Several samples of the known $KReO_4$ solution were treated to verify this fact. Each sample had the same rhenium content, but the acid concentration was varied. The solution which was 0.5 N in hydrochloric acid

reacted very poorly to a hydrogen sulphide precipitation. The precipitation was not quantitative. In the case of the solution 2.5 N in hydrochloric acid the rhenium was precipitated only after a long time and did not appear very complete. The solution, which was 33 per cent acid, gave a rapid and complete precipitation. It was also accompanied by the characteristic color change of pink to purple to black. The precipitate was very black and flocculant. There was no difficulty encountered in filtering it.

Investigation then centered on the precipitation of the sulphide in the 33 per cent hydrochloric acid solution. 100 grams of the flue dust were treated in the above manner. The characteristic color changes shown by the known rhenium solution did not occur. Some sulphur and a small amount of arsenic sulphide was precipitated. The sulphides were dissolved in nitric acid, and the sulphur filtered off. The solution was evaporated down slowly to dryness and the residue taken up with water and a little hydrochloric acid. The solution was then neutralized with potassium hydroxide and a colorimetric analysis made on it. Here again the results were negative.

In order to verify the previous tests, some rhenium was put in the flue dust to see if it could be recovered. In this the precipitation of the rhenium was characteristic and complete. The rhenium content was equal to 0.1 per cent in the prepared sample, but there is no doubt that the presence of 1/10 or even 1/100 as much rhenium could have been detected.

The flue dust from Great Falls was also treated with

hydrogen sulphide in the strong acid solution. More difficulty was encountered here in getting a sulphide precipitate, since much sulphur was thrown out of solution.

The sulphide precipitates from this flue dust were also prepared and tested by the colorimetric method of Analysis. In this no indication of rhenium could be obtained. Very low known concentrations of rhenium gave very definite indications by this method.

VIII. Conclusions

In conclusion it must be stated that there is no indication of the presence of rhenium in either of the flue dusts.

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X. Bibliography

(1) Mellor, J. W. - Comprehensive Treatise On Inorganic and Theoretical Chemistry Vol. 12

(2) U. S. B. M. - Information Circular No. 6475 (1931)

(3) Fink, Colin G. and Deren, P. - Rhenium Plating-Trans. Electrochemical Soc. - 66, P 471-474, (1934)

(4) Yogoda, Herman - Detection of Rhenium in the Sodium Carbonate Bead - Ind. and Eng. Chem. (Anayl. Ed.) 8, No. 2, P 133 (1936)

(5) Snell, F. D. & C. T. - Colormetric Methods of Analysis 2nd Ed. (1936)

(6) Hurd, Loren C. - The Determination of Rhenium - Ind. and Eng. Chem. (Analy. Ed.) 1 & 2, P. 11-15, 112-114 (1936)

(7) Hardy, C. - Rhenium and Masurium-J. Ind. Eng. Chem. (news Ed.) - 9, 208 (1931)

(8) Roth, Walter - Potassium Perrhenate Recommended for the Determination of Rhenium - Ind. & Eng. Chem. (News Ed.)- 8, 7, (1930)

(9) Noyes and Bray - System of Qualitative Analysis of the Rarer Elements - (1927)

(10) McAlpine and Soule - Prescott's and Johnson's Qualitative Chemical Analysis

(11) Hurd, Loren C. - The Discovery of Rhenium - J. Chem. Ed. - 10, 605 (1933)

(12) Feit, Wilhelm - The New Element Rhenium - Ind. and Eng. Chem. (New Ed.) 9,122, (1931)

(13) Müller, J. H. and La Lande, W. A. Jr. - The Precipita-

tion of Rhenium Sulphide from Ammonical Solution.- J. Am. Chem. Soc. 55, 2376 - 78, (1933)

(14) Yost, D. M. and Shull, G. O. - The Density and Molecular State of Rhenium Tetrachloride and Rhenium Hexachloride in the Gaseous State. J. Am. Chem. Soc. - 54, 4657-59 (1934)

(15) Chem. Abs. - 24, 560-561, (1930)

(16) Chem Abs. - 25, 387, (1931)

(17) Chem. Abs. - 25, 2930, (1931)